Near-infrared electronic spectrum of \( \text{CH}_2^+ \)

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Four vibronic bands of the \( \tilde{A} \, ^2B_1(\Pi_u) \rightarrow \tilde{X} \, ^2A_1 \) electronic transition of \( \text{CH}_2^+ \) have been observed in the near infrared from \( \sim 11 \text{,}000 \text{–} 13 \text{,}000 \text{ cm}^{-1} \) using a highly sensitive spectrometer based on a Ti:sapphire laser and a positive column plasma. The two states are derived from the lowest \( ^2\Pi_u \) state of the linear conformation as a result of a strong Renner–Teller effect. As expected, the rovibronic structure of the CH\(_2^+\) spectrum is very similar to that of the isoelectronic BH\(_2\) radical reported by Herzberg and Johns. Results of a preliminary analysis are given in which the rotational structures of the two states are treated independently, the ground state as a near-prolate asymmetric rotor and the excited state as a linear molecule. © 2004 American Institute of Physics.

Methylenecation, CH\(_2^+\), is one of the most fundamental radical carbocations and has been well known in mass spectroscopy since its early days.\(^1\) Although it has been the subject of numerous kinetic studies,\(^2\) its spectroscopic studies have been rather limited because the extremely high chemical reactivity makes it difficult to produce CH\(_2^+\) in sufficient quantities in laboratory plasmas. The first spectrum of CH\(_2^+\) was reported by our group in 1992 as the infrared vibration–rotation spectrum of the \( v_2 \) band, where only the \( K_u = 0 \) series was observed.\(^3\) Subsequently we observed the \( K_u = 1 \) series with spin-rotation fine structure which was analyzed by Jensen et al.\(^4\) Those parallel bands (\( \Delta K_u = 0 \)) have provided accurate values of the \( B \) and \( C \) rotational constants and established the quasilinear \( C_{2v} \) structure of CH\(_2^+\) in the ground electronic state. More recently, the zero-kinetic-energy (ZEKE) photoelectron spectroscopy conducted in Merkt’s laboratory has determined the \( A \) rotational constant through the analysis of perpendicular (\( \Delta K_u = 1 \)) as well as parallel bands and led to the experimentally determined zero-point structure of \( r_{CH} = 1.049(41) \text{Å} \) and \( a_{HCH} = 139.77(27)^\circ \)\(^5\)\(^,\)\(^6\), which is in agreement with the \( ab \, initio \) calculations.

In this paper, we report the first observation of an electronic transition of CH\(_2^+\) in the near infrared at \( \sim 0.9 \mu \text{m} \). As expected, the spectrum is similar to that of isoelectronic BH\(_2\) radical studied by Herzberg and Johns.\(^7\) The absorption is from the slightly bent ground \( \tilde{X} \, ^2A_1 \) state to the linear first excited \( \tilde{A} \, ^2B_1(\Pi_u) \) state. The levels are derived from the \( ^2\Pi_u \) state of the linear conformation as a result of a strong Renner–Teller interaction. There have been several \( ab \, initio \) calculations on the fascinating energy level system of CH\(_2^+\).\(^8\)-\(^10\) In particular, recent papers by Bunker, Jensen and colleagues\(^4\)-\(^11\)-\(^13\) have provided very accurate \( ab \, initio \) calculations.

As before,\(^3\) CH\(_2^+\) was produced by Penning ionization of CH\(_4\) in a helium-dominated (CH\(_4\):He \( \sim 1:100 \) with a total pressure of \( \sim 10 \text{ Torr} \)) liquid-nitrogen-cooled positive-column AC plasma at 19 kHz with a current of \( \sim 200 \text{ mA} \) rms. In order to achieve high sensitivity our near-infrared spectrometer incorporates velocity modulation, phase modulation with heterodyne detection, bidirectional optical multipassing, and dual-beam subtraction. The experimental setup is nearly identical to that previously described,\(^14\) except that custom software has been designed to interface with Coherent’s Autoscan software in order to provide greater flexibility in the laser control as well as significantly improved data acquisition capabilities. We scanned the entire wavelength range of our Coherent 899 titanium:sapphire ring laser in search of CH\(_2^+\) transitions using the midwavelength optics set (\( \sim 11 \text{,}000 \text{–} 13 \text{,}000 \text{ cm}^{-1} \)).

In order to discriminate between the CH\(_2^+\) lines and the thousands of absorption lines from unidentified cationic species, we use chemical discrimination. With the addition of 100 mTorr of \( \text{H}_2 \) to the plasma, the CH\(_2^+\) lines uniformly decreased in intensity by a factor of \( \sim 3 \) due to the hydrogen abstraction reaction that forms CH\(_3^+\) at the Langevin rate of \( 2 \times 10^{-9} \text{ cm}^{-3} \text{ s}^{-1} \).

We have identified four vibronic bands, three of which have been assigned as the \( \tilde{A}(0,3,0)^1 \rightarrow \tilde{X}(0,0,0)^0 \), \( \tilde{A}(0,3,0)^2 \rightarrow \tilde{X}(0,0,0)^1 \), and \( \tilde{A}(0,4,0)^0 \rightarrow \tilde{X}(0,0,0)^1 \) transitions based on the calculated subband origins of Osmann et al.\(^12\) and one to the \( \tilde{A}(0,3,0)^3 \rightarrow \tilde{X}(0,0,0)^2 \) transition based on the prediction by Bunker et al.\(^13\) The three numbers in parentheses are quantum numbers of the three normal modes \( \nu_1 \), \( \nu_2 \), and \( \nu_3 \) and superscripts are rovibronic angular momentum \( K \) along the (quasi-) linear axis. The four bands are \( \Pi \rightarrow \Sigma, \Delta \rightarrow \Pi, \Sigma \rightarrow \Pi, \) and \( \Phi \rightarrow \Delta \) type perpendicular transitions and the excited states are \( (0,8,0)^1 \), \( (0,9,0)^2 \), \( (0,9,0)^0 \), and \( (10,0,0)^3 \) in the notation of Pople and Longuet-Higgins,\(^15\) which was used by Herzberg and Johns\(^7\) in the analysis of BH\(_2\). Using the ground state combination differences obtained from our infrared spectrum,\(^3\)\(^,\)\(^4\) the rotational assignments of three of the vibronic bands are complete.
The observed CH$_2$$_1$ spectrum is qualitatively identical in its rovibronic structure to that of BH$_2$ except that the higher resolution of our laser spectrometer has allowed us to resolve the spin-rotation fine structure. The size of the spin splitting varies from $\sim 0.06$ cm$^{-1}$ to more than 7 cm$^{-1}$. Stick diagrams of the simplest and strongest $\tilde{A}(0,3,0)\rightarrow\tilde{X}(0,0,0)^0$ band and the more complicated $\tilde{A}(0,3,0)^2\rightarrow\tilde{X}(0,0,0)^1$ band are shown in Fig. 1. Unassigned lines that mimic the behavior of the lines assigned to CH$_2$$_1$ (i.e., similar linewidths and decrease in intensity with the addition of H$_2$) are also included in Fig. 1. The strongest line observed in all four bands

\begin{table}[h]
\begin{tabular}{cccccc}
\hline
Upper State & Band & $v_k^{(0)}$ & $\Gamma^*$ & $B'_{\text{eff}}$ & $10^3\times D'_{\text{eff}}$ \\
\hline
\hline
(0,8,0) & $\Pi \rightarrow \Sigma$ & 11 140.921(92) & $\Pi^+$ & 7.1560(78) & $-1.75(57)$ \\
(0,9,0) & $\Sigma \rightarrow \Pi$ & 12 243.838(54) & $\Sigma^-$ & 6.8306(55) & $-16.06(99)$ \\
$\Delta \rightarrow \Pi$ & 12 138.532(98) & $\Delta^+$ & 6.9411(83) & 1.24(70) \\
(0,10,0) & $\Phi \rightarrow \Delta^*$ & 12 920(10) & $\Phi^-$ & 6.8908(98) & 9.31(69) \\
\hline
\end{tabular}
\end{table}

*This band has not yet been rotationally assigned.
has a S/N of \( \sim 55 \). The \( \tilde{A}(0,3,0)^3 - \tilde{X}(0,0,0)^2 \) band is extremely weak and only a few lines are strong enough to be observed after the addition of \( \text{H}_2 \) to the plasma.

Like Herzberg and Johns, we analyzed rotational structures of the two electronic states independently—the ground state as a very nearly prolate asymmetric rotor \((A \approx B \approx C)\) and the excited state as a linear molecule. Table I lists the ground state rotational constants from this experiment, along with those from previous experiments. Preliminary values of subband origins \( v_k^{(D)} \), rotational constants \( B_{\text{eff}} \), and centrifugal distortion constants \( D_{\text{eff}} \) for the excited state \( \tilde{A}^2B_1 \left( ^2\Pi_u \right) \) are listed in Table II. The numbers in parentheses indicate the uncertainty for each constant (one standard deviation). Rotational energy levels have been calculated for the ground state using the observed\(^6 \) value of \( A = 67.65 \text{ cm}^{-1} \) and the observed ground state combination differences. Upper state energy levels were obtained by adding the wavenumbers of the observed lines to the lower state energy levels. The spin splitting has been neglected and averaged values of the two spin components have been used in the least-squares fitting. A more detailed analysis of the assigned bands including spin splitting as well as an analysis of the \( \tilde{A}(0,3,0)^3 - \tilde{X}(0,0,0)^2 \) band is in progress.

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